SUPERCRITICAL WATER OXIDATION OF WASTEWATER FOR MILITARY APPLICATIONS

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ABSTRACT

Supercritical Water Oxidation (SCWO) is based on the unique properties of water at conditions near and beyond its thermodynamic critical point of 374°C and 22 MPa. SCWO involves carrying out oxidative reactions in the supercritical water environment in the presence of an oxidant, typically air or pure oxygen. At typical SCWO reactor conditions of 650°C and 23.5 MPa, densities are less than one tenth that of normal liquid water and the properties are similar to high-pressure steam. Steam, organic vapors and oxidant become dispersed within a single phase which, in conjunction with the high diffusivity, low viscosity, and relatively dense SCW reaction medium, is conducive to rapid oxidation reactions. The temperature is sufficiently high that complete reaction is usually attained in 10 to 20 seconds. Rapid reaction rates have been demonstrated for virtually all types of organic materials, including solids. Extremely clean liquid and gaseous effluents can be produced by the process, with negligible formation of harmful byproducts such as nitrogen oxides, sulfur dioxide, or dioxins.

SCWO has been under development by the Air Force (AF), Army, DARPA/ONR and commercial industry for the destruction of hazardous materials. Applications of the technology for use in the destruction of waste streams from conventional and chemical demilitarization operations are being pursued. A SCWO unit has been installed at the US Army Defense Ammunition Center (DAC) for testing. Testing of simulants and real waste streams from conventional demilitarization operations has been successfully completed. Testing has also been performed at General Atomics (GA) using a SCWO system developed under DARPA/ONR and AF programs with other waste streams of interest to the military. Several new SCWO systems are being designed and constructed by GA. Major advancements are being made in the technology as these units are being fielded and as testing continue.

The SCWO process is extremely flexible and amenable to numerous waste streams generated by military related activities including smokes and dyes, activated carbon and black/grey water wastes all of which have been successfully processed by GA SCWO systems. This paper documents the results of a test program focusing on SCWO of Redwater waste streams utilizing the GA SCW Test Unit.

PURPOSE

There has been no new TNT production in the United States since the Radford Army Ammunition Plant, VA, ceased production 15 years ago, and the huge stockpile accumulated prior to that shutdown has been nearly exhausted. The AF estimates it will require TNT supplies until at least 2007, after which it may eliminate TNT as a warhead fill in favor of less sensitive explosives. The military is currently pursuing options for resuming manufacture of TNT. One key environmental issue it must face when TNT production is resumed is how to dispose of the Redwater waste stream in an efficient and environmentally responsible manner. The EPA classifies TNT Redwater as RCRA hazardous waste K047 due to its reactivity. One of the traditional methods of disposal is incineration. However, incineration can be costly and frequently involves lengthy and complicated permitting issues and is sometimes viewed as an environmentally unfriendly technology. SCWO offers a new approach that is an economical and environmental friendly alternative to incineration. SCWO provides a solution for the Redwater hazardous waste disposal problem.

TEST PROGRAM GOALS

The goals of the Redwater SCWO testing program were:

- Demonstration of high organic destruction efficiencies
- Demonstration of continuous reactor salt transport
- Demonstration of stable process control
- Characterization of process effluents
- Investigation of the behavior of materials of construction exposed to the SCWO environment
- Development of a processing database to assist in the potential future design of a full scale Redwater waste SCWO system

PROCESS DESCRIPTION

The GA SCWO process for hazardous waste destruction typically utilizes temperatures and pressures of water above its critical point of 374°C and 22.1 MPa (705°F, 3208 psia) to break down hazardous organic materials to carbon dioxide, water and other innocuous compounds. The treatment is applicable to a broad range of organic compounds as well as oxidizable inorganic species such as ammonia and cyanide. Key to the success of the process is the fact that gases, including oxygen, and organic substances are completely soluble in supercritical water, whereas inorganic salts exhibit greatly reduced solubilities under process conditions. The effluents from the process are clean water; gas consisting of CO_2, O_2, and sometimes N_2O; and solids if the waste contains inorganic salts or organics with halogens, sulfur, or phosphorus. The water is often clean enough to discharge directly to the environment without further treatment. The gas contains little or no NO_X, acid gases (SO_2, HCL), or particulates, and less than 10 ppm carbon monoxide.

The GA SCWO process typically consists of the following general processing steps:

<u>FEED AND PREHEATING</u>

1. Process water and a suitable oxidant are pressurized, heated as required and delivered to the reactor.
2. A suitable fuel is introduced into the reactor to initiate the oxidation reaction.

3. Waste feed material is delivered to the reactor. Fuel and/or process water flowrates are adjusted to maintain the desired reactor temperature, typically between 600°C and 700°C.

REACTION AND SALT TRANSPORT

1. Organics are oxidized in a controlled, but rapid reaction. The heat released by the readily oxidized components is sufficient to raise the fluid phase to temperatures at which all organics are oxidized.
2. Salts present in the waste feed stream or produced from the reaction transport, as solids, and flow to the reactor bottom where they are re-solubilized in the quenched effluent stream.
3. Quench water is introduced at the reactor bottom to rapidly cool the oxidized effluent to below the critical temperature.

PRESSURE LETDOWN

1. The cooled effluent from the process separates into a liquid water phase and a gaseous phase, the later containing primarily nitrogen (when air is the oxidant), carbon dioxide and oxygen which is in excess of the stoichiometric requirements.
2. Pressure letdown of the phases is carried out in multiple stages in order to minimize erosion of pressure control elements.
3. Gaseous and liquid phases are typically separated in a moderate pressure gas-liquid separator vessel.

GA SCW TEST UNIT DESCRIPTION

The GA SCW Test Unit as configured for the Redwater testing program is comprised of 3 transportable skids and various associated support equipment. A brief description of the major equipment items and their role in the Redwater testing program follows.

CLEAN FEED SKID

The clean feed skid contains the tankage, pumping, delivery and control equipment for the de-ionized water and fuel utilized in the SCWO process. Positive displacement, piston style pumps are utilized for the high pressure delivery of these fluids to the reactor skid. All pumps are equipped with spring loaded pressure safety relief valves.

The flowrate of each fluid is continuously controlled via motor speed rate adjustment from the computer control system. Water pumps are of the fixed stroke length, simplex variety and utilize turbine style flowmeters for flowrate measurement. The triplex fuel pump has independent, local stroke length adjustment for each head. A mass flow meter is used to continuously measure the fuel flowrate.

The clean feed skid also houses the high pressure reactor liner gas purge delivery and control module. This module contains a pneumatically driven gas compressor, high pressure gas storage vessel, pressure control regulators, gas flowmeter and pressure and temperature instrumentation. Nitrogen gas was used as the liner purge media for all Redwater tests performed under this program.

All electrical controls, motor contactors and instrument interfaces for the equipment associated with this skid are contained within an electrical box mounted on the skid.

REACTOR SKID

The reactor skid comprises the heat-up, reaction, cooldown and letdown equipment associated with the SCWO process.

A 250 KW ohmic style heater was used to heat high pressure water to bring the reactor to oxidizing conditions. The computer control system (CCS) interfaced ohmic heater package included 17.6 ft^2 of heat transfer area and all required electrical conditioning, instrumentation and safety equipment.

The reactor utilized in the Redwater testing program consisted of a vertical, high pressure/high temperature shell with water cooled, O-ring sealed end closures, a removable insulated liner and a corrosion resistant, Ti-2 floating liner. The nominal reactor process ID for all Redwater testing was 3.28". The reactor process length to inside diameter (L/D) ratio was ~ 18.

Feed materials including Redwater, air and fuel are mixed in a nozzle prior to their introduction into the SCWO reactor.

A small flowrate of nitrogen was metered into the annular gap between the removable liner OD and reactor shell ID for all Redwater tests. This purging fluid prevents potentially corrosive reactor contents from migrating onto the reactor shell walls. Additionally, the purge fluid cools the reactor shell allowing higher reaction temperatures without exceeding the allowable temperature rating of the vessel wall.

Reacted fluid was quenched with DI water. Dilute NaOH was automatically metered into the effluent for pH control during the later Redwater experiments. Reactor instrumentation included four internal, Type K thermocouples with Ti-2 sheaths. The thermocouples were positioned at various reactor elevations to asses the extent of the oxidation reaction and reactor salt transport.

The reactor effluent was cooled to near room temperature in a series of single tube-in-shell, coiled heat exchangers. The cooling media was a water and glycol solution circulated in a heat transfer loop cooled by a standard, evaporating type cooling tower.

Cooled, two phase reactor effluent was letdown from ~ 3400 psig to ~ 1500 psig through a CCS controlled flow control valve (FCV). The rate of fluid letdown controlled the reactor pressure. A gas-liquid separator (GLS) vessel allowed nearly complete separation of the gas and liquid phases. The pressure of the GLS was controlled by a manually set back pressure regulator. The liquid level within the GLS was controlled by a CCS interfaced FCV.

WASTE PUMPING AND ANALYTICAL SKID

The waste pumping and analytical skid contains the equipment utilized to pump and deliver waste feeds to the reactor as well as various on-line analytical equipment used to monitor critical aspects of the SCWO process.

Redwater feed was delivered to the SCWO reactor with a duplex, positive displacement diaphragm metering pump. The feed pump has both variable stroke length and motor speed capabilities to allow precise metering of the feed material to the reactor. Stroke length was manually controlled locally. Speed control was remote via the CCS. The Redwater feed was gravity feed to the pump from a 100 gallon, stainless steel tank.

On-line analytical analyses for the Redwater testing program included O_2, CO_2 and CO for the gaseous effluent and pH and conductivity for the liquid effluent.

AIR COMPRESSOR AND AIR DELIVERY

All Redwater tests utilized air as the oxidant. A commercially available, high pressure (5000 psig) reciprocating compressor was employed to pressurize atmospheric air to the desired pressure. A CCS interfaced FCV metered the high pressure air to the reactor at the desired flowrate. The high-pressure air flowrate was monitored by an orifice plate coupled to a DPT interfaced with the CCS.

COMPUTER CONTROL AND DATA AQUISITION

The GA SCW Test system is provided with a semi-automatic control system. The system provides real-time control of a variety of process parameters, allowing the operator to concentrate on monitoring the SCW system performance. The computer control system (CCS) consists of four major functional parts: instrumentation, control elements, programmable logic controller (PLC) and the supervisory computer system.

Instrumentation includes sensors to measure temperature, pressure, flow rate, chemical composition and other critical processing parameters. Control elements include on-off valves, control valves, regulators, pump variable speed drives, heater power controllers and other process interfacing equipment.

The PLC is capable of performing complete system control independent of the supervisory computer system. It performs critical system functions including data acquisition from all instrumentation, sequential logic control for alarms and interlocks, implementation of control loop strategies and control of all control elements. The supervisory computer system provides the operator interface to the system.

The CCS system I/O count numbers approximately 175 points. There are approximately 12 automated control loops including oxidant flowrate control, reactor temperature control, system pressure control, and heater temperature control.

PROGRAM TEST MATRIX

Table 1 presents an overview of the tests performed during this program including preliminary testing with Redwater simulants. Initial tests with simulants and actual Redwater were performed for short durations to assess critical engineering parameters and to fine tune the process conditions and critical computer control elements. The final test was performed for 21 hrs to assess longer term SCWO operability issues during Redwater processing.

Table1

GA Test #	Feed	Fuel	Feed Duration (Hrs)	Feed Flowrate (g/min)	Reactor Temperature (^oC)	Reactor Pressure (psi)
SCW-26	16%Na_2SO_3	Diesel	2	625	650	3400
SCW-27	16%Na_2SO_3	Diesel	2.5	425 600	650	3400
SCW-28	16%Na_2SO_3	Diesel	6	600	650	3400
SCW-29	16%Na_2SO_3	Diesel	2	600	650	3400
SCW-33.1	16%Na_2SO_3	Ethanol	3	300	700	3400
SCW-33.1	Redwater	Ethanol	3.5	150 300	700	3400
SCW-34	Redwater	Ethanol	3.5	300	700	3400
SCW-35	Redwater	Ethanol	4	300	700	3400
SCW-37	Redwater	Ethanol	2	50	750	3400
SCW-38	Redwater	Ethanol	7.5	50 to 300	750	3400
SCW-39	Redwater	Ethanol	5.75	300	725	3400
SCW-40	Redwater	Ethanol	8.5	300	725	3400
SCW-41	Redwater	Ethanol	21	300 to 350	750	3400

FEED MATERIALS

Numerous feed materials were utilized during the Redwater testing program. This section describes these materials and their use in the program.

REDWATER

GA obtained four fifty-five gallon drums (~ 816 Kg net) of Redwater taken from an Australian TNT manufacturing facility in mid October, 2002. GA received the hazardous material under the provisions of the State of California's treatability study regulations as treatability study samples.

Redwater results from the purification of the 2,4,6 TNT isomer during manufacture of the TNT. After full nitration, the raw molten TNT product is counter-currently contacted with a 16 wt% solution of sodium sulfite (Na_2SO_3). The undesirable isomers and other byproducts such as DNT react with the sodium sulfite and become soluble in water. The 2,4,6 TNT remains relatively insoluble and is purified as the byproducts are dissolved in the aqueous stream. The aqueous waste stream retains the 16 wt% sodium sulfite reacted with ~ 8 wt% TNT byproducts in solution. Thus, the waste is an aqueous solution containing ~ 8 wt% organic that produces ~ 18 wt% sodium sulfate (Na_2SO_4), prior to quenching, when oxidized in the SCWO reactor.

The Redwater waste was shipped in standard closed top carbon steel drums. Due to treatability study quantity limitations on storage, only two drums were allowed on site at any one time. The excess material was housed at a local, certified hazardous waste storage facility until required by GA for testing. The drums were stored at the GA facility, per regulation, on secondary containment pallets when not required by the testing schedule. GA performed chemical analyses on the as received Redwater to better define its composition. Table 2 presents the results of some of these analyses. All results are in mg/L.

Table 2

Sample	TOC	Mg	Na	Cr	Fe	Mo	Ni	Ti
A-1	22,500	36.7	23,600	Note 1	Note 1	Note 1	Note 1	Note 1
A-2	19,800	33.0	21,600	0.28	86.1	<0.05	0.34	<0.05
B-1	19,800	34.1	20,700	Note 1	Note 1	Note 1	Note 1	Note 1
B-2	18,000	32.8	21,100	Note 1	Note 1	Note 1	Note 1	Note 1

Notes 1. A-2 values assumed typical for all samples

The presence of moderate quantities of iron (Fe) in the Redwater is believed to result from the corrosion of the drums containing the material during shipping and storage at GA.

SIMULANT FEED MATERIALS

Initial testing utilized SCWO feed materials intended to simulate the inorganic constituents and their concentrations expected in actual Redwater waste materials. The material of primary interest is $NaSO_3$ which is used extensively in the purification of TNT.

OTHER FEED MATERIALS

Fuel is required to obtain the desired reactor operating temperatures due to the low heating value of the Redwater waste material. Initial testing utilized diesel fuel while later tests utilized 100% ethanol.

Air was utilized as the oxidizer for the SCWO process for the Redwater testing program. A commercially available, high pressure compression system was rented for the duration of the testing. A GA designed and fabricated air introduction system was utilized to control the air flowrate to the reactor.

De-ionized water was utilized as the quenching fluid. A dilute solution of NaOH was metered into the quench water during the later tests. The NaOH is used to neutralize the quenched reactor effluent to a pH of between 5 and 10.

TESTING RESULTS

The initial experimental runs utilized simulant materials to define effective SCWO processing boundaries including cold feed injection (CFI) conditions, organic destruction, fuel type, control system configuration and reactor salts transport. Later experimental runs utilized actual Redwater waste with a salt transport additive. The remainder of this section focuses on the final, long duration experimental run (SCW-41) which represents the culmination of all the previous testing.

The liquid analytical results from SCW-41 are presented in two segments of the 21 hour test separated by a ~ 3 hour shutdown. Table 3 presents the liquid effluent analyses from each of the steady state periods. Liquid samples were collected once per hour during steady state operation. A composite of the hourly samples from each segment was prepared to generate a single sample for analyses. The stated values, therefore, represent an average of the results for the given run segment. All results are in mg/L of the composited liquid effluent.

Table 3

	TOC	pH	Na	SO_4	Fe	Cr	Mg	Ni	Ti
Segment 1	0.8	6.89	6820	8190	1.44	0.14	3.81	0.13	0.05
Segment 2	0.6	6.36	15000	10500	3.09	0.14	5.63	0.28	0.08

The SCWO gaseous effluent was continuously monitored with on line analyzers. Additionally, grab samples of the gaseous effluent during steady state operation were collected for analysis by an outside, EPA certified laboratory. Table 4 presents the results of these analyses.

Table 4

N_2 (%)	CO_2 (%)	O_2 (%)	CO (ppmv)	H_2 (ppmv)	CH_4 (ppmv)	H_2SO_4 (mg/m^3)	SO_2 (mg/m^3)	NO_x (mg/m^3)
85.1	8.8	6.1	<13*	< 340*	<13*	< 0.01*	< 0.01*	<3.8*

* Compounds were not detected. Minimum detection limit value reported.

SUMMARY

GA performed thirteen experimental runs between the October, 2002 and February, 2003 utilizing the SCW Test Unit during this Redwater testing program. Initial experiments processed Redwater waste simulants tailored to match the salt species and concentrations (~ 16 wt% sodium sulfite) anticipated with actual Redwater. Later experiments utilized actual Redwater waste material obtained from an operational TNT production plant. The initial experiments generated the critical data needed to configure the SCW test system and optimize the processing conditions for the successful treatment of Redwater. Initial Redwater runs were of short duration to allow further fine tuning of the process parameters. Additionally, these shorter runs provided liquid and gaseous samples for analytical analysis to confirm effective processing parameters. The program culminated in a twenty one hour test to confirm the applicability of the SCWO process for extended duration Redwater processing.

The Redwater testing program demonstrates that the GA SCWO process is suitable for the effective treatment of Redwater waste. Liquid effluents contain less than 1.0 ppm total organic carbon (TOC) and consist primarily of water and dissolved salts. Gaseous effluents contain less than 13 ppmv CO and less than 4.0 mg/m^3 of NO_X.

The SCWO process temperatures and pressures are controllable and stable while processing Redwater waste for extended durations. Reliable salt transport and minimal metallic corrosion are achieved treating Redwater waste materials with the GA SCWO process.

All SCWO processed effluents were directly discharged to the environment with no further treatment.

The high levels of inorganic salts present in and produced from the oxidation of the Redwater waste stream did not pose operational problems. During SCW-41 approximately 376 Kg of raw Redwater were processed. Assuming an average Na concentration of 21,750 mg/L and that all Na present in the raw Redwater produces Na_2SO_4, a total of 23 Kg of the salt was produced. Given a total reactor volume of ~ 8,800 cm^3 and a pure salt density of 2.069 g/cc, a total of 1.26 reactor volumes of pure salt were produced. This simple analysis provides a very conservative example as, in practice, the salts generated during the SCWO process are typically much lower in density than the pure, crystalline form. Also, a reduction in reactor volume due to salt deposition will have a significant impact on residence time leading to poor organic oxidation performance. The described test demonstrates that this was not an issue because the salts were transported through the system. Other operational problems resulting from reactor salt deposition can include unstable process temperatures and pressures neither of which was observed during SCW-41. Finally, the liquid effluent conductivity remained relatively constant for the duration of the test indicating that reactor salt transport equilibrium was achieved and maintained.

The liquid effluent metal analysis data did not indicate the presence of significant quantities of metallic corrosion products which suggests that corrosion may not be an issue when processing Redwater wastes.

The data and experience gained from the SCWO Redwater program provides a significant database for the potential future design of a full scale processing facility. The successes experienced during the program indicate that the GA SCWO process has significant potential for the demanding mission of continuous Redwater processing.